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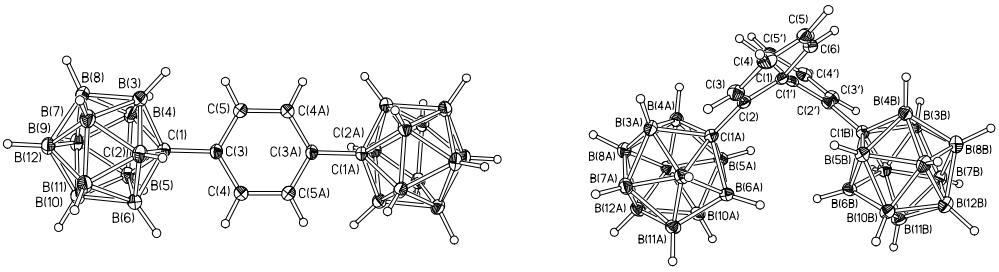
Graphical Abstract



Studies on bis(1'-*ortho*-carboranyl)benzenes and bis(1'-*ortho*-carboranyl)biphenyls

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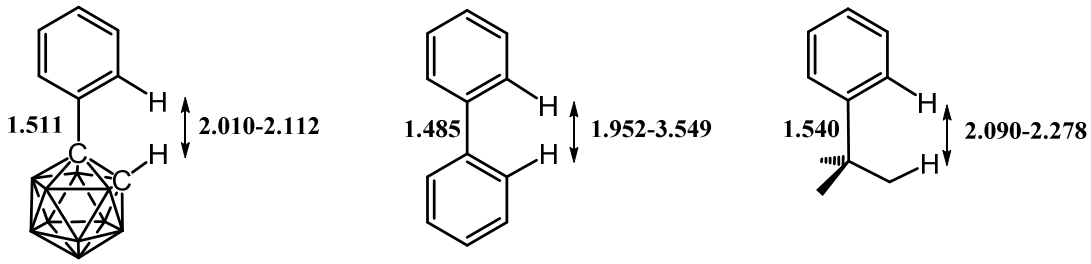
Abstract

Reactions between the C,C'-dicopper(I) derivative of *ortho*-carborane and *ortho*-, *meta*- and *para*-diiodobenzene are reported. The reaction with 1,2-$C_6H_4I_2$ unexpectedly afforded 2,2'-bis(1'-*ortho*-carboranyl)biphenyl, $[HCB_{10}H_{10}CC_6H_4]_2$ **2**, whereas reactions with 1,3- or 1,4-$C_6H_4I_2$ provided alternative routes to 1,3-bis(1'-*ortho*-carboranyl)benzene **3** and 1,4-bis(1'-*ortho*-carboranyl)benzene **4** respectively. The crystal structure of the biphenyl derivative **2** revealed significant distortions in the biphenylene framework attributable to the proximity of the two bulky carborane cages. UV absorption spectra and electrochemical data on **2** and **3** showed little electronic communication between the two carborane cages in either, and negligible pi-conjugation between the two *ortho*-phenylene rings in **2**. However, substantial evidence was found of electronic communication between the carborane cages via the *para*-phenylene bridge in **4**. B3LYP/6-31G* computations have been carried out on compounds **2** and **4**, on 4,4'-bis(*ortho*-carboranyl)biphenyl **6** and on 1,2-bis(1'-*ortho*-carboranyl)benzene **7**. Those on **2**, **4** and **6** show the computed geometries to be in very good agreement with the experimental geometries: those on **7** allowed the reported molecular geometry of this compound to be revised and revealed a long cage C-C bond of 1.725(3)A.

Introduction

Ever since icosahedral carboranes were first made in the 1960s,[1] their stabilities, 5-coordinate carbon atoms, derivative chemistry and bulk have attracted considerable interest.[2] Icosahedral carboranyl residues as substituents have larger cone angles and occupy slightly larger volumes than fully rotating phenyl groups,[3-6] as illustrated by B3LYP/6-31G* optimized geometries of 1-phenyl-*ortho*-carborane **1**,[7,8] biphenyl[7,9] and *tert*-butylbenzene,[9] the ranges of H...H nonbonded intramolecular interactions in which are shown in Fig. 1. Our own interest in such systems stemmed from our use of *meta*- or *para*-phenylene links (or indeed 2,6-disubstituted pyridine rings) to connect together *ortho*-, *meta*- or *para*-icosahedral carboranes in diamond-shaped or hexagonal arrays.[10,11]

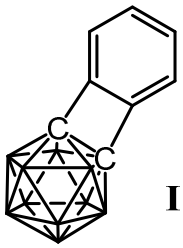


1

Figure 1. Comparison of C-C bond and range of shortest H(cage)…H(Ar) intramolecular distances in angstroms (Å) on rotation of the phenyl group in optimised geometries of phenyl-*ortho*-carborane **1**, biphenyl and *tert*-butylbenzene. Each naked vertex in **1** represents BH.

Generally, C-aryl-*ortho*-carboranes can be made by two routes, from decaborane and arylalkynes[4,5,10,12-18] or by copper-mediated coupling of *ortho*-carborane with iodo aryls.[19,20] The latter route, however, results only in C-monoaryl-*ortho*-carboranes in many cases.[19] Conversely, the copper-mediated coupling of *ortho*-carborane with 2-bromopyridine gave only the disubstituted product, 1,2-(2'-pyridyl)$_2$-1,2-$C_2B_{10}H_{10}$. One explanation for this may be that the proximity of the nitrogen atom in the non-isolable intermediate 1-(2'-pyridyl)-1,2-$C_2B_{10}H_{11}$ facilitates the second C-C coupling.

In the present work, we hoped the reaction of the dicopper(I) derivative of *ortho*-carborane with 1,2-diiodobenzene would form product I in which a 4-membered ring connected an *ortho*-phenylene residue to the carborane cage (Chart 1). Carborane derivatives of this type are already known.[21] However, the crowded biphenyl derivative **2** bearing carborane cages adjacent to the link between the benzene rings was obtained instead. (Figure 2) The separate reactions of the dicopper(I) derivative of *ortho*-carborane with *meta*- and *para*-diiodobenzene were also studied and found to generate the biscarboranyl benzenes **3** and **4** respectively. (Figure 3) Structural, photophysical, electrochemical and computational studies on these systems are described below.



I

Chart 1. Target carborane **I**

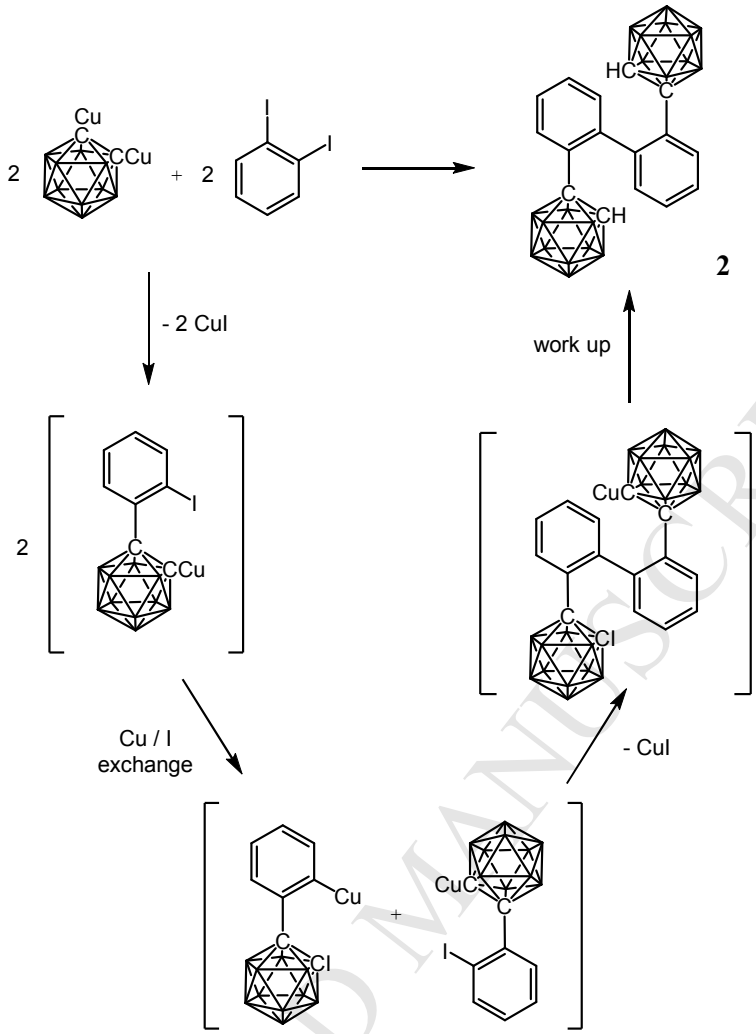
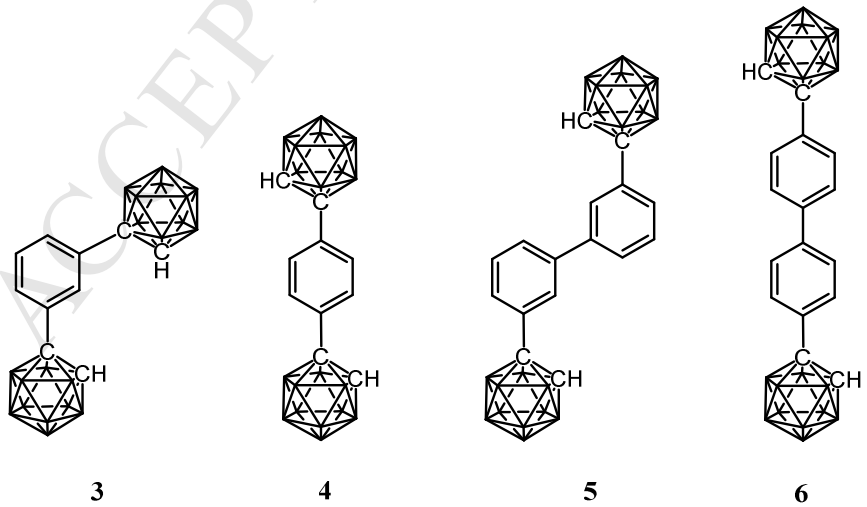


Figure 2. Formation of the biphenyl **2** and the proposed reaction pathway.



3 **4** **5** **6**

Figure 3. Reactions of 1,2-$Cu_2C_2B_{10}H_{10}$ with 1,3- or 1,4-diiodobenzenes gave compounds **3** or **4** instead of **5** or **6** respectively.

Results and Discussion

The reaction between the dicopper(I) derivative of *ortho*-carborane and 1,2-diiodobenzene in a 1:1 ratio gave the di-*ortho*-carboranylbiphenyl **2**, instead of the target compound **I**, as the main carborane product (Figure 2). The unexpected two-cage compound **2** was identified by mass spectrometry, infrared and detailed NMR spectroscopy. Formation of the aryl-to-aryl bond in the biphenyl **2** presumably results from an Ullmann reaction of an arylcopper derivative following exchange of one iodine atom with copper, plausibly in the initial intermediate, C-iodophenyl-*ortho*-carborane. It is inferred that under these constrained conditions copper-iodine exchange becomes a significant pathway.

The reactions of the dicopper(I) derivative of *ortho*-carborane with 1,3- or 1,4-diiodobenzenes afforded 1,3-bis(1'-*ortho*-carboranyl)benzene **3**[5,12,13] or 1,4-bis(1'-*ortho*-carboranyl)benzenes **4**[12] respectively (Figure 3). The biphenyls that may be expected based on the formation of **2**, i.e. 3,3'-bis(*ortho*-carboranyl)biphenyl **5** and 4,4'-bis(*ortho*-carboranyl)biphenyl **6**,[16] were not obtained. This suggests that the copper-iodine exchange is not a significant step in the iodophenyl-*ortho*-carborane intermediate in these reactions.

X-ray crystallography

Crystal structures of the two carborane assemblies, **2** and **4**, were determined by X-ray crystallography here while carborane **3** has been structurally determined elsewhere.[13] Substantial distortions in the biphenylene skeleton are found in the crystal structure of the two-cage biphenyl **2** as expected from steric crowding by the bulky carboranyl substituents on the two-ring frame at the *ortho* positions to the aryl-aryl link (Figure 4). The two rings retain planarity with the twist angle between the two rings at 70.2 º. Examination of the bond distances and angles in the biphenylene framework reveals that the bonds are not distorted but the angles between the cages and the aryl-aryl link, 124-6 º, are widened to accommodate the two bulky cages in **2** (Figure 5). Crystal structures of related biphenyls with one *ortho*-carboranyl group at the 2-position do not show such large angles.[3,22]

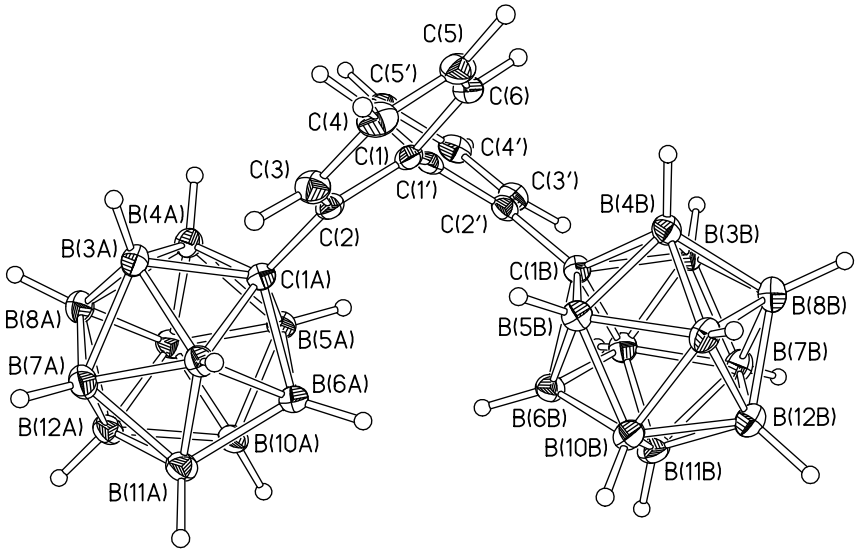


Figure 4. Molecular structure of the biphenyl **2**. The unlabelled cluster atoms bonded to C(1A) and C(1B) are the carbon atoms C(2A) and C(2B) respectively.

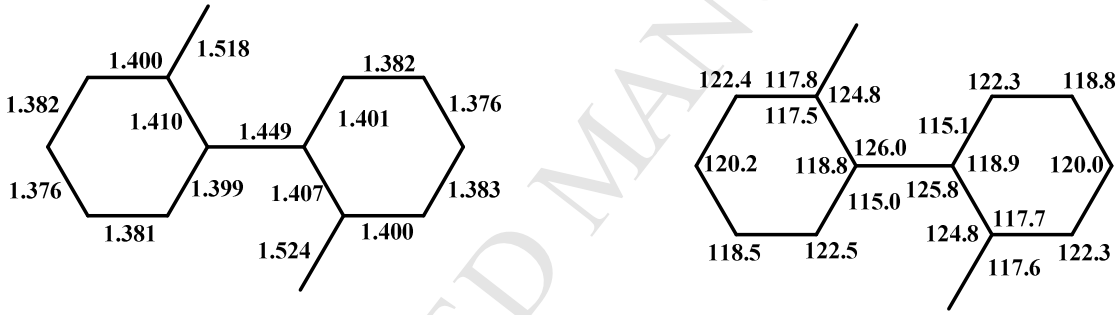


Figure 5. Bond distances (Å, left) and angles (º, right) of the distorted biphenylene framework in the crystal of **2**. The bond distances have estimated standard deviations (e.s.d.s) of 0.002 Å and angles have e.s.d.s of 0.2 º.

The carboranyl groups in **2** are ordered with the CH positions located. The cage ordering in both compounds **2** and **4** is probably facilitated by intermolecular cage C-H…H-B interactions (Figure 6).[23] The C…B distances in these interactions are 3.86 and 3.94 Å for **2** and 3.93, 3.74 and 3.75 Å for **4**.

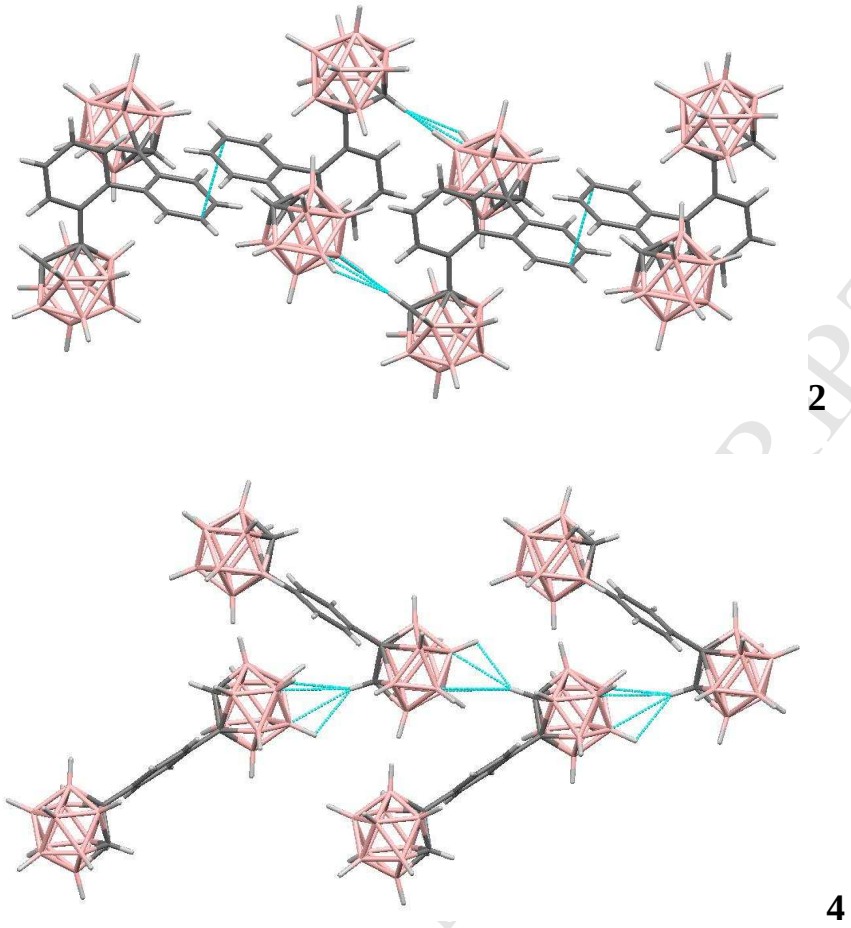


Figure 6. Crystal structures of **2** and **4** with short intermolecular interactions shown in blue.

The cage C(1A)-C(2A) and C(1B)-C(2B) bonds are determined to be somewhat long at 1.669(2) and 1.683(2) Å despite the low values of torsion angles, θ, [C(3)-C(2)-C(1A)-C(2A)] and [C(3')-C(2')-C(1B)-C(2B)] around C(ring)-C(cage) bond equal to 22.9º and 26.9º respectively. A cage C-C bond length of around 1.64 Å is expected when the torsion angle θ is small.[15] In the reported crystal structures of **1,** the cage C-C bonds are 1.640(5) and 1.649(2) Å with the torsion angles θ of 18.3º and 22.3º respectively.[24] In the crystal structure of **2** the C(4')-C(5') bonds of benzene rings of adjacent molecules are antiparallel with the shortest interatomic C…C(1-x,-y,1-z) distance of 3.40 Å, that probably indicates the presence of π…π interactions (Figure 6).

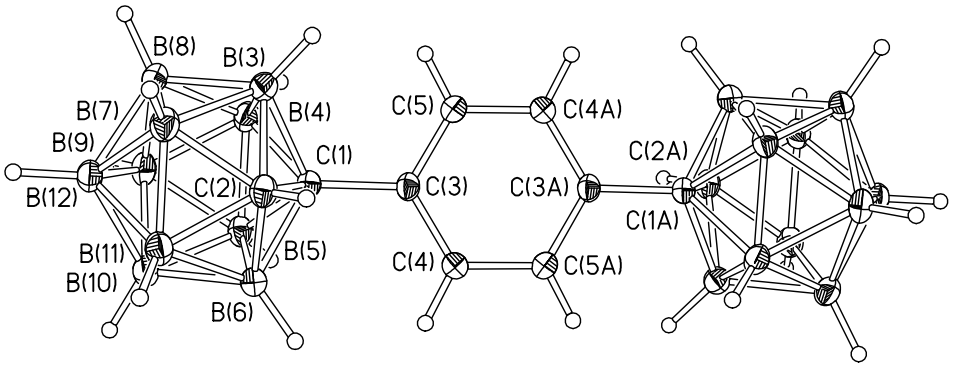


Figure 7. Molecular structure of **4**. Selected bond lengths in Å, C(1)-C(3) 1.5084(13), C(3)-C(4) 1.3950(13), C(3)-C(5) 1.3928(14), C(4)-C(5A) 1.3897(13).

The molecule in crystal structure of **4** has an inversion centre at the centre of the *para*-phenylene ring (Figure 7). The cage C(1)-C(2) bond is 1.6591(13)Å which is expected for a large torsion angle θ of 79.6º. The parameters within the *para*-phenylene framework of **4** are similar to the crystal structures of related derivatives, 1,4-bis[1'-(2'-methyl-*ortho*-carboranyl)]benzene,[25] 1,4-bis[1'-(2'-phenyl-*ortho*-carboranyl)]benzene[26] and 1,4-bis[1'-(2'-benzyl-*ortho*-carboranyl)]benzene.[12]

Electrochemistry

The cyclic voltammogram (CV) for phenyl-*ortho*-carborane **1** has an irreversible 2-electron reduction wave at -2.25 V (Figure 8, Table 1) as reported elsewhere.[27] The current intensity on the oxidation wave at -1.66 V after reduction is only half the intensity of the reduction wave and the peak-to-peak separation between the two waves is 590 mV.

The presumed 4-electron irreversible reduction waves in the CV traces for biphenyl **2** and the 1,3-phenylene compound **3** are observed at reduction potentials of -1.87 and -1.90 V respectively. These values indicate that **2** and **3** are more easily reduced than **1**. The oxidation waves observed after reduction are closer in current intensities as the reduction waves with anodic peak – cathodic peak separations of 310 and 270 mV for **2** and **3** respectively. These values suggest improved stabilities of the tetraanions formed from **2** and **3** compared to the dianion formed from **1**.

A very different CV trace is seen for the *para*-phenylene compound **4** with two distinct waves. The two waves in **4** suggest that the dianion $[\mathbf{4}]^{2-}$ is formed followed by the tetraanion $[\mathbf{4}]^{4-}$ on reduction. The stability of the dianion $[\mathbf{4}]^{2-}$ is promoted by the *para*-phenylene bridge where electronic communication between the two carboranyl groups is present.[28]

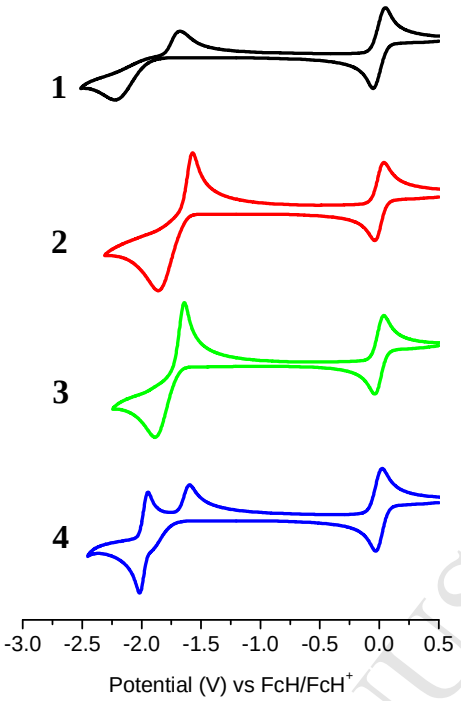


Figure 8. Cyclic voltammograms for **1-4** in acetonitrile. The traces are stacked for clarity. The waves at $E_{1/2}$ = 0.0 V are ferrocene/ferrocenium couples arising from the internal ferrocene references.

Table 1. Cyclic voltammetry data for **1-4** with a glassy carbon working electrode in acetonitrile and scan rate of 100mV/s. Values in italics correspond to anodic waves of the species formed on rearrangement, reaction or decomposition of the initial reduced species.

		E^c V	E^a V	$E_{1/2}$ V	E^a-E^c mV	E^c V	E^a V	$E_{1/2}$ V	E^a-E^c mV
1	2e waves	0 to -2	-2 to 0						
		-2.25	*-1.66*		*590*				
2	4e waves	0 to-4	-4 to 0						
		-1.87	*-1.56*	*-1.72*	*310*				
3	4e waves	0 to -4	-4 to 0						
		-1.90	*-1.63*	*-1.77*	*270*				
4	2e waves	0 to -2	-2 to 0	0/-2		-2 to -4	-4 to -2	-2/-4	
		-1.93	-1.58	-1.76	350	-2.02	-1.79	-1.91	90

UV spectroscopy

The UV absorbance spectrum of 1-phenyl-*ortho*-carborane **1** shows weak bands with fine structure between 260 and 272 nm corresponding to the benzene-type forbidden π → π* transition known as the *B* band (Figure 9).[29] A strong band is also seen at < 225 nm which is assigned to the allowed π → π* transition as the *E*-band. The small bathochromic shifts in these bands for **1** compared to benzene are attributed to the inductive electron-withdrawing influence of the carboranyl group.

The UV spectra of the carboranyl biphenyl **2** and the *meta*-phenylene assembly **3** are similar to that of **1** indicating a lack of conjugation between the two rings[30] in **2** and between the two cages in **3**. The absorption spectrum for **4** reveals bands present at 227-241 nm which are at considerably longer wavelengths than the *E* bands in the spectra of **1**-**3**. This suggests a greater degree of conjugation with the two carboranyl groups in the *para*-phenylene bridge of **4** than in the bridges of **2** and **3**. The bands at 227-241 nm for **4** may arise from allowed π → π* transitions with considerable carborane character in these orbitals.

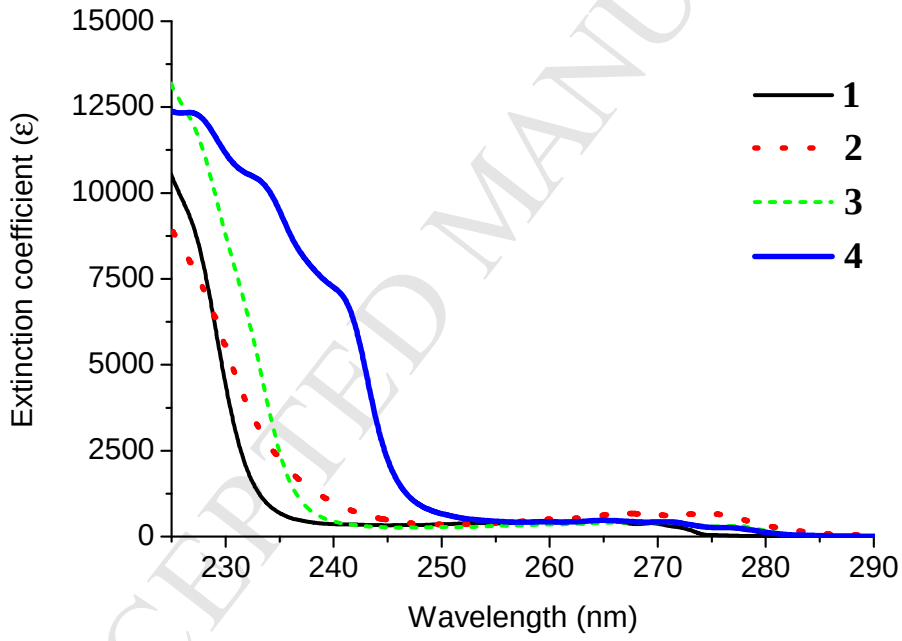


Figure 9. Solvent-corrected absorbance spectra of **1**-**4** in cyclohexane.

Computations

Geometry optimisations of the two-cage assemblies **2**, **4** and **6** were carried out at B3LYP/6-31G* to compare with their experimentally determined geometries where their cage CH positions were located.[16] The C1-C2 bond lengths and the torsion angles, θ, for these computed and experimental geometries are listed in Table 2. There is very good agreement in all cases which show confidence in the accuracy of the optimised geometries at B3LYP/6-31G*.

Table 2. Comparison of selected parameters in the optimised and experimental geometries of carboranes **2**, **4** and **6**.

	C1-C2 bond length (Å)		Torsion Angles, θ (°)	
	Calculated	Observed	Calculated	Observed
2	1.669	1.669(2), 1.683(2)	27.0	22.9, 26.9
4	1.669	1.6591(13)	91.4	79.6
6	1.647	1.634(8), 1.643(7)	34.2	10.2, 26.7

The assembly 1,2-bis(1'-*ortho*-carboranyl)benzene **7** is an isomer of **3** and **4** and the reported crystal structure has a highly distorted benzene ring due to two adjacent carboranyl groups (Figure 10).[4,5] The non-equivalent clusters were denoted cage A and cage B. The reported experimental values of 1.700 Å and 1.657 Å for C(1A)-C(2A) and C(1B)-C(2B) bond lengths respectively were initially surprising given that the positions of both carbons C(2A) and C(2B) are similar and both θ torsion angles are small at 5.4 and 14.7 °. As boron and carbon atoms are difficult to distinguish by X-ray crystallography there is the possibility of the carboranyl carbon atoms in **7** being incorrectly located.[23] Another possibility is that the carboranyl groups may be disordered in the structure of **7** as found in crystal structures of **1** and **3**.

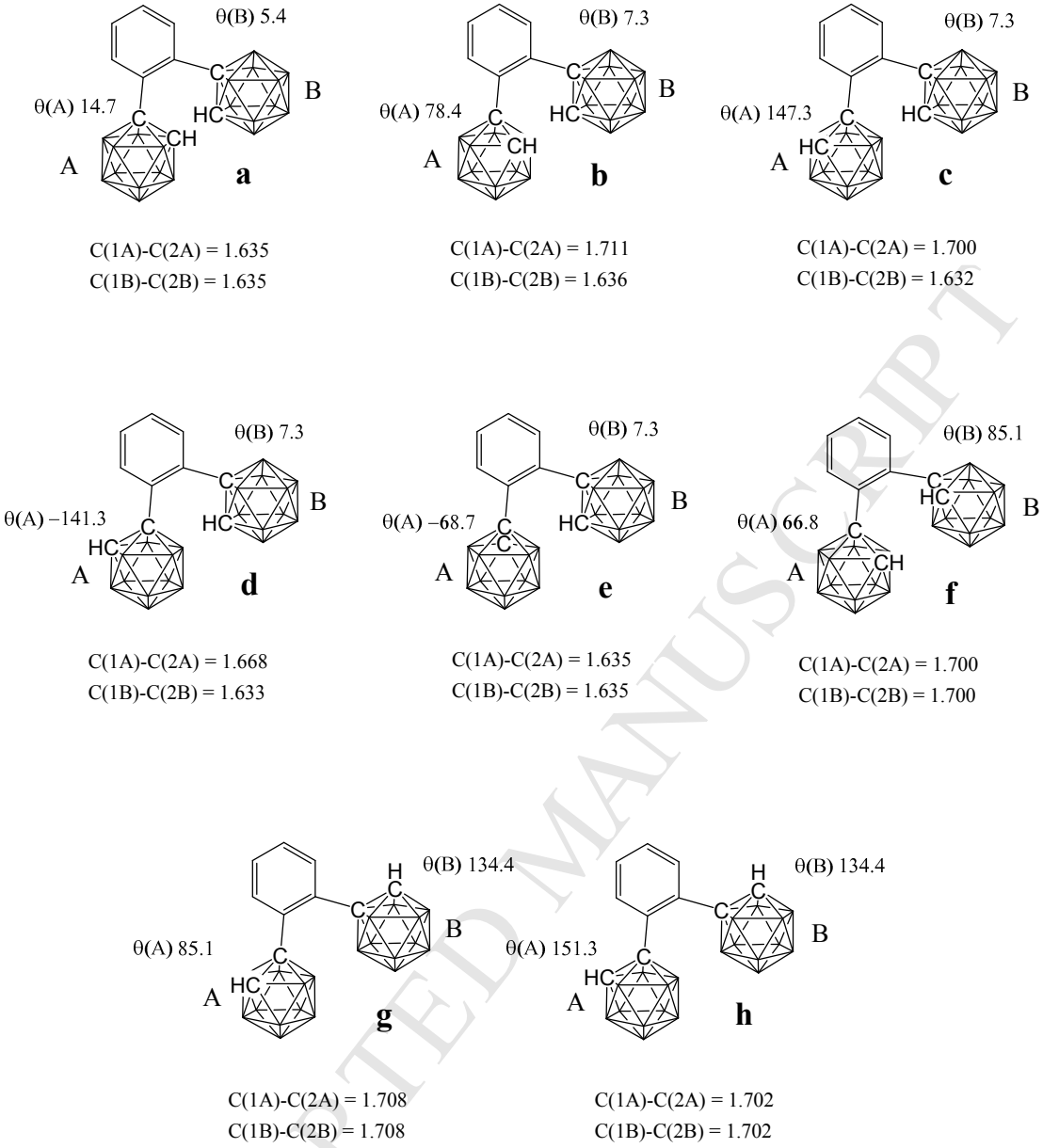


Figure 10. Starting conformers **a**-**h** with initial torsion angles θ in degrees (°) for geometry optimisations of **7** and the C1-C2 bond distances in Å after optimisations.

Geometry optimisation of **7**, based on the reported experimental geometry, as the starting geometry (conformer **a**, Figure 10) gave a geometry with equivalent carboranyl groups. Given this discrepancy with the reported data, geometry optimisations were carried out on other possible conformers of **7** i.e. **b** to **h.** The optimised geometries for conformers **b**, **c** and **d** contained non-equivalent carboranyl groups whereas the optimised geometries for **e**, **f**, **g** and **h** had equivalent carboranyl groups. Optimisation of conformer **e** resulted in the same geometry as conformer **a**. Geometry optimisations carried out at the computationally-intensive electron-correlated wavefunction method MP2/6-31G* for conformers **a**, **b**, **c** and **d** confirmed the validity of the geometries optimised at the hybrid DFT method B3LYP/6-31G*.

The best-fit (r.m.s.) or misfit procedure,[15,23] using the ofit command in XP within the SHELXTL package,[31] was applied between the experimentally determined molecule of **7** and the four MP2-optimised conformers **a**-**d**. The lower the misfit value (Å) is calculated, the better the fitting is. It is clear from Table 3 that conformer **b** fits best with the experimental data. The fitting value of 0.0057 Å confirms the position of C(2B) in cage B whereas the fitting value of 0.0234 Å for cage A suggests the likely position for C(2A).

Table 3. Best fit values between the experimental geometry for **7** and the optimised geometries of conformers **a**-**d** and the relative energies of the optimised geometries at MP2/6-31G*.

	Cage A heavy-atom fitting (Å)	Cage B heavy-atom fitting (Å)	Relative Energy (kcalmol^{-1})
Conformer **a**	0.0432	0.0161	0.0
Conformer **b**	0.0234	0.0057	1.6
Conformer **c**	0.0510	0.0166	0.2
Conformer **d**	0.0525	0.0166	2.9

It is concluded here that the geometry in Figure 11 is the correct one in the crystal structure of **7**. Close cage C-H…X intermolecular interactions were observed for B(9B)-H…H-C(2A) at 2.28 Å and B(9B) … C(2A) at 3.86 Å promoting cage order in the carboranyl groups in the crystal structure (Figure 12). An interesting observation in this revised geometry is that the C(1A)-C(2A) distance is even longer at 1.725(3) Å. This is a remarkably long C1-C2 bond for a monosubstituted *ortho*-carborane and is in fact a typical value for a diaryl-*ortho*-carborane.[14,16] The long C(1A)-C(2A) bond is clearly due to the considerable steric influences of the benzene ring and the neighbouring cage. The C2-C1-C(1A)-C(2A) θ angle of 85.1 ° may also have a subtle electronic effect on the lengthening of the bond.

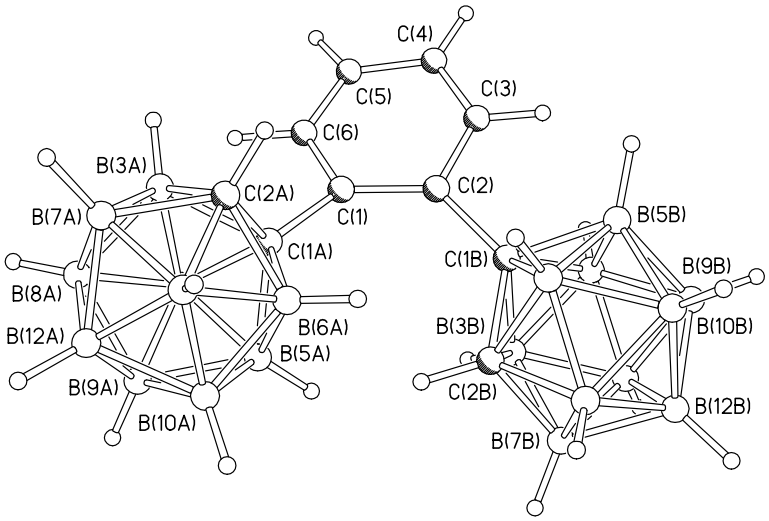
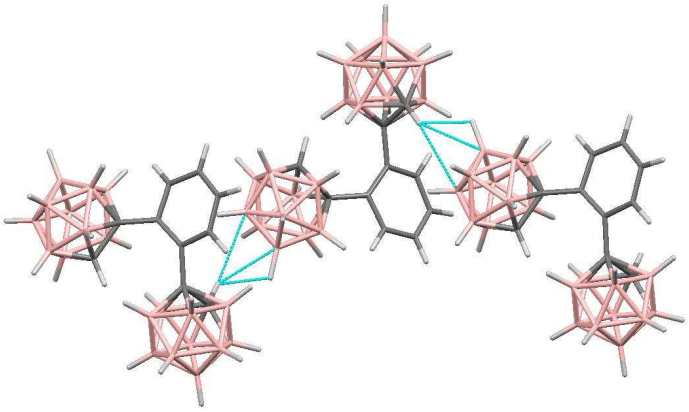


Figure 11. Revised molecular structure in the crystal structure of **7** with the cage carbons C(2A) and C(2B) correctly located.



7

Figure 12. Revised crystal structure of **7** with short intermolecular interactions shown in blue.

The relative energies for the four conformers **a-d** of **7** are listed in Table 3. Conformer **b** is slightly higher in energy compared to conformers **a** and **c** by 1.4-1.6 kcalmol^{-1} but it is likely that conformer **b** exists in the crystal structure (instead of conformer **a** and **c**) due to favourable intermolecular interactions in the crystal (Figure 12). Using conformer **a** for **7**, the relative energies between **7** and the benzene isomers **3** and **4** reveal that 7 is 28.6 and 29.2 kcalmol^{-1} higher than **3** and **4** respectively. These substantial energy differences reflect the unfavourable distortion of the phenylene framework caused by the bulky carboranyl groups in **7**. The energy differences between the biphenyls **2** and **5** and between **2** and **6** are 21.0 and 21.4 kcalmol^{-1} respectively with **2** higher in energy than **5** and **6**. These values indicate that the steric effects of the carboranyl groups at the 2-,2'- positions on the biphenylene framework in **2** are less significant compared to those in **7**.

Electronic structure computations carried out on the optimised geometries of **1**-**7** revealed that compounds **2**-**7** with two carboranyl groups have LUMO energies over 0.5 eV lower than 1-phenyl-*ortho*-carborane **1** (Figure 13). This is in accord with the observed reduction potentials in the CV data for **1**-**4** (Table 1). The LUMOs for all compounds **1**-**7** are on the aryl rings with carboranyl group contributions in the range of 9-31 % (Figure 13). The HOMOs are also on the aromatic rings with cage contributions of 3-26%.

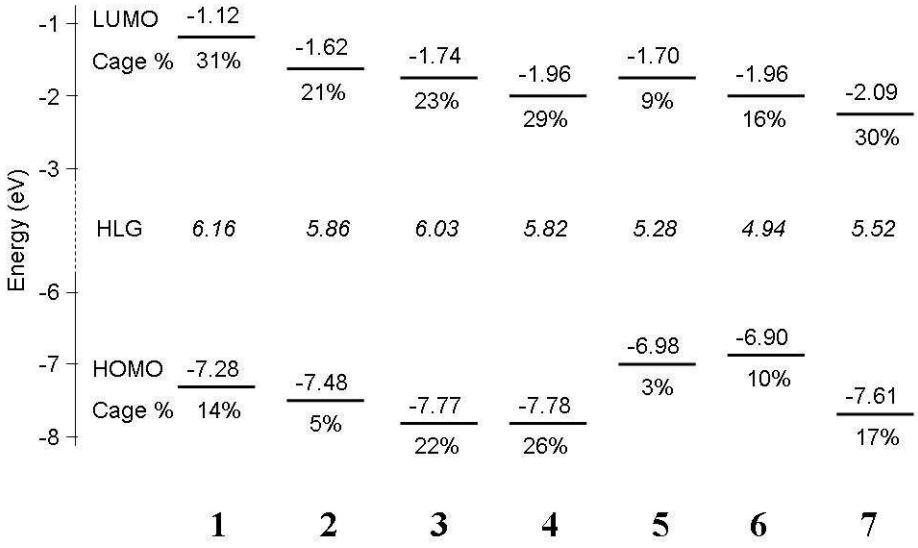


Figure 13. Comparison of the frontier orbital energies in **1**-**7**. HLG = HOMO-LUMO Gap energy.

The *para*-phenylene assembly **4** has the highest cage character in its frontier orbitals (29% LUMO, 26% HOMO, Figure 14) of the compounds studied here. This suggests a degree of communication between the two carboranyl groups as shown by electrochemical and photophysical data compared to the related isomer **3**. TD-DFT data at B3LYP/6-31G* on optimised geometries of **3** and **4** predicted HOMO → LUMO transitions with high oscillator strengths (*f*) at 204 nm (*f* = 1.0501) for **3** and at 229 nm (*f* = 0.6145) for **4**. The predicted TD-DFT data are in general agreement with observed absorption spectra for **3** and **4** (Figure 9).

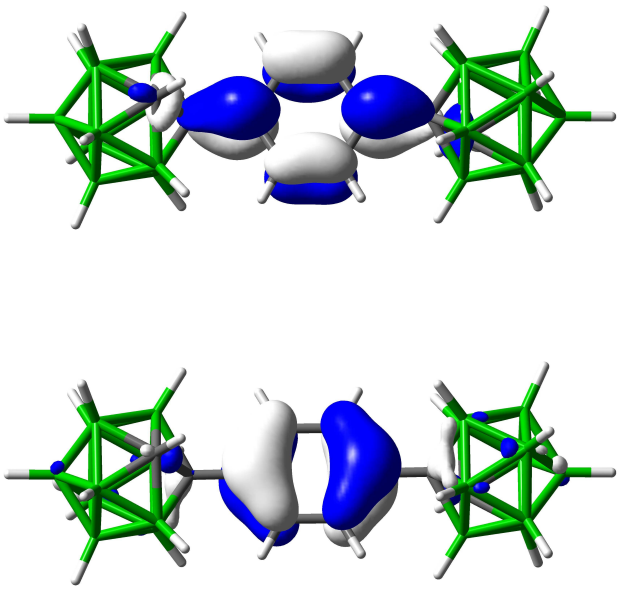


Figure 14. Frontier orbitals for **4**.

Conclusions

A biphenyl molecule with two carboranyl groups at the 2,2'-positions was unexpectedly formed from *ortho*-carborane and 1,2-diiodobenzene via the copper-mediated coupling procedure. By contrast, reactions with 1,3- and 1,4-iodobenzenes in place of 1,2-diiodobenzene afforded benzenes (rather than biphenylenes) with two attached carboranyl groups. The molecular geometry in the crystal structure of benzene with two carboranyl groups at 1,2-positions was revised on the basis of conformational analyses and geometrical fittings. From the electrochemical and absorption data, the benzene with carboranyl groups at the 1,4-positions showed evidence of electronic communication between the two cages.

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Experimental Section

Dimethoxyethane was dried by distillation from potassium and pyridine by distillation after standing over potassium hydroxide. Copper(I) chloride was purified by the method of Whitesides[32] and stored under nitrogen. Infrared spectra were recorded as KBr discs on a Perkin Elmer 1600 series FTIR. Background corrected and solvent corrected UV-Vis absorption spectra were recorded from cyclohexane solutions in quartz cells with a 1 cm path length on an ATI Unicam UV / VIS UV2 spectrometer. GC-MS mass spectra were recorded on a Thermo-Finnigan Trace mass spectrometer. NMR spectra were measured in $CDCl_3$ solution except where stated using Varian Unity-300 (^{1}H, ^{11}B, ^{13}C), Bruker AM250 (^{1}H, ^{13}C) and/or Varian Inova 500 (^{1}H, ^{11}B)

instruments. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^{1}H NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm). ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$ 77.0 ppm). ^{11}B NMR spectra were referenced externally to $BF_3{\cdot}Et_2O$ at 0.0 ppm. Peak assignments for the carborane clusters were aided by 2D ^{11}B-^{11}B{^{1}H} COSY and ^{1}H{^{11}B-selective} spectra. Electrochemical measurements were carried out with an Autolab PG-STAT 30 using dry acetonitrile solutions containing 0.1 M NBu_4PF_6 electrolyte in a standard three-electrode cell with a glassy carbon (2 mm) working electrode and platinum wires as counter and reference electrodes. Chromatographic silica refers to Merck Art. No. 9385. Phenyl-*ortho*-carborane **1** was made by a literature procedure.[33] UV (λ/nm, ε) for **1**: 260 (500), 265 (500), 269 (400), 272 (300).

2,2'-Bis(1-*ortho*-carboranyl)biphenyl **2**

Under nitrogen, a solution of *ortho*-carborane (1.44 g, 10 mmol) in dimethoxyethane (40 cm^3) was treated dropwise with butyllithium (16.0 cm^3, 1.31 M in hexanes) and pyridine (6.0 cm^3) was added followed by copper(I) chloride (2.2 g). The dark red mixture was heated to bath temperature 90˚C and distilled in a slow stream of nitrogen until 16 cm^3 of distillate had collected, 1,2-diiodobenzene (0.95 cm^3) was added and the solution was kept at 90˚C for 40 h. Ether (280 cm^3) was added to the cooled solution which was filtered after 2 days. The filtrate was washed with dilute hydrochloric acid (80 cm^3, 2 M) and water (600 cm^3; 3x200 cm^3), dried and evaporated. The oily residue (2.06 g) was dissolved in ether, evaporated with chromatographic silica (6.0 g) and eluted through a column of silica (25 g) with benzene. The first fraction (50 cm^3) was evaporated under vacuum, sublimed under high vacuum to remove *ortho*-carborane (0.52 g) and triturated with cyclohexane to give the biphenyl derivative **2** as a chalky white solid (326 mg, 0.7 mmol, 18 %). Recrystallization from cyclohexane and then from butan-1-ol gave crystals suitable for X-ray crystallography. M.p. 216-217 °C. Found: C, 43.3; H, 6.9. $C_{16}B_{20}H_{30}$ requires: C, 43.3; H, 6.9. IR (ν_{max}/cm^{-1}): 3086m (carboranyl CH); 2646s, 2587vs (BH stretch); 1472m; 1430w; 1278w; 1160w; 1127w; 1070m; 1021m; 1002m; 792m; 759s; 738m; 490w. UV (λ/nm, ε): 261 (500), 268 (700), 275 (700). δ^{1}H{^{11}B}: 7.76 (2H, d, J 8, C3,3'H), 7.44 (2H, t, J 8, C4,4'H), 7.36 (2H, t, J 8, C5,5'H), 7.09 (2H, d, J 8, C6,6'H), 3.54 (2H, cage CH), 2.52 (4H, B3,6H), 2.28 (4H, B9,12H), 2.25 (4H, B4,5H), 2.16 (4H, B8,10H), 2.04 (2H, B7H or B11H), 1.95 (2H, B11H or B7H). δ^{13}C{^{1}H}: 137.6 (C1,1'), 134.1, 132.8, 130.7 (C2,2'), 129.4, 128.4, 76.4 (cage C-aryl), 59.2 (cage CH). δ^{11}B: -2.6 (4B, d, J 153, B9,12); -9.0 (8B, d, B4,5,8,10); -10.5 (4B, d, B3,6); -13.1 (4B, d, J 164, B7,11). EI-MS: 428-442, 438.33 100%, M$^+$; 287-297, 294.19 68% $C_{14}H_{21}B_{10}^+$.

1,3-Bis(1-*ortho*-carboranyl)benzene **3**

A similar method was carried out as for the synthesis of **2** except that 1,3-diiodobenzene was used instead of 1,2-diiodobenzene. After sublimation of *ortho* carborane, the 1,3-bis(1-*ortho*-carboranyl)benzene was purified by passing through a column of silica and eluting with hexane to give the white solid product **3** (182 mg, 0.5 mmol, 10 %). M.p. 256 °C. Found C: 30.16; H, 7.27. $C_{10}B_{20}H_{26}$ requires: C, 32.75; H, 7.15. IR: (ν_{max}/cm^{-1}): 3061w (carboranyl CH), 2574s (BH stretch); 1490w; 1430w; 1350w; 1172w; 1073m; 1013m;, 1001m; 936w; 814m; 721m; 688s; 602m; 552m; 526m; 464m.UV (λ/nm, ε): 266 (400), 271 (400), 277 (300). δ^{1}H{^{11}B}: 7.65 (1H, s, aryl C2H), 7.49 (2H, dd, J 8.0, 1.9, C4,6H), 7.31 (1H, t, J 8.0, C5H), 3.90 (2H,

s, cage CH), 2.56 (4H, s, B3,6H), 2.44 (6H, s, B4,5,9H), 2.34 (6H, s, B8,10,12H), 2.28 (4H, s, B7,11H). $\delta^{13}C\{^1H\}$: 134.4 (C), 129.4 (CH_c), 128.9 (CH_b), 127.7 (CH_a), 75.2 (cage C), 60.1 (cage CH). $\delta^{11}B$: -1.7 (2B, d, J 151, B9), -3.9 (2B, d, J 151, B12), -8.7 (4B, d, J 151, B8,10), -10.8 (4B, d, J 172, B4,5), -11.5 (4B, d, B3,6), -12.6 (4B, d, J 152, B7,11). EI-MS: 350-365, 362.32 100%, M^+.

1,4-Bis(1-*ortho*-carboranyl)benzene **4**

An identical procedure was carried out as for the synthesis of **2** except that 1,4-diiodobenzene was used instead of 1,2-diiodobenzene. After the unreacted *ortho* carborane was sublimed, the 1,4-bis(1-*ortho*-carboranyl)benzene **4** was purified by column chromatography eluting with hexane to give the white solid (241 mg, 0.75 mmol, 13 %). This was recrystallised from dichloromethane to give colourless crystals suitable for X-ray crystallography. M.p. 317 °C. Found: C, 32.50; H, 7.18. $C_{10}B_{20}H_{26}$ requires: C, 32.75; H, 7.15. IR: (ν_{max}/cm^{-1}): 3072s (carboranyl CH); 2650m, 2600s, 2575s, 2557s (BH stretch); 1508m; 1407s; 1194w; 1164w; 1071s; 1038m; 1002m; 920m; 873m; 847s; 729s; 717s; 571s; 503s. UV (λ/nm, ε): 227 (12,400), 233 (10,400), 241 (7,000), 265 (500), 271 (400), 277 (300). $\delta^1H\{^{11}B\}$: 7.45 (4H, s, aryl CH), 3.92 (2H, cage CH), 2.54 (4H, B3,6H), 2.45 (6H, B4,5,9H), 2.32 (6H, B8,10,12H), 2.27 (4H, B7,11H). $\delta^{13}C\{^1H\}$ 135.2 (aryl C-cage C), 128.1 (aryl CH), 74.9 (cage C-aryl C), 59.9 (cage CH). $\delta^{11}B$: -1.8 (2B, d, J 150, B9); -4.0 (2B, d, J 156, B12); -8.7 (4B, d, J 153, B8,10); -10.8 (8B, d, B4,5,3,6), -12.5 (4B, d, J 164, B7,11). EI-MS: 350-365, 362.33 100%, M^+.

X-ray crystallography

The single crystal X-ray data were collected at 120K on the Bruker SMART-CCD 1K (compound **2**) and Bruker SMART-CCD 6000 (**4**) diffractometers (λMoKα, λ = 0.71073Å, ω-scan, 0.3°/frame) equipped with Cryostream (Oxford Cryosystems) open-flow nitrogen cryostates. The structure were solved by direct method and refined by full-matrix least squares on F^2 for all data using SHELXTL[34] and OLEX2[35] software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were located on the difference map and refined isotropically. Crystal data and experimental details are given in Table 4. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 930976 and 930977.

Table 4. Crystal data and refinement parameters for compounds **2** and **4**

Compound	**2**	**4**
Empirical formula	$C_{16}H_{30}B_{20}$	$C_{10}H_{26}B_{20}$
Formula weight	438.60	362.51
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	13.614(4)	6.8195(2)
b/Å	8.111(2)	12.6682(3)
c/Å	22.783(6)	12.3936(3)
β/°	100.705(7)	104.20(2)
Volume/$Å^3$	2472.0(12)	1037.98(5)
Z	4	2
ρ_{calc}/mg mm^{-3}	1.179	1.160
μ/mm^{-1}	0.054	0.051
F(000)	904	372
Reflections collected	27729	12326
Independent reflections	6122 [R_{int} = 0.0681]	2755[R_{int} = 0.0281]
Goodness-of-fit on F^2	1.027	1.090
Final R_1 index [I>2σ (I)]	0.0501	0.0501
Final wR_2 index [all data]	0.1257	0.1440

Computational Section

All computations were carried out with the Gaussian 09 package.[36] The geometries were optimized at B3LYP/6-31G* with no symmetry constraints. Frequency calculations were computed on these optimized geometries and confirmed them to be true minima. For conformer **a**, the experimental geometry **7** was used as the starting geometry with the unsubstituted carboranyl atoms C(2A) and C(2B) at the positions shown in Figure 10. The conformers **a**-**d** were also carried out at the computationally intensive MP2/6-31G* level to confirm the results obtained at B3LYP/6-31G*. Time-dependent DFT (TD-DFT) were carried out on the optimized geometries of **3** and **4** at B3LYP/6-31G*. The MO contributions were generated using the GaussSum package.[37]

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Supporting Information

Studies on bis(1'-*ortho*-carboranyl)benzenes and bis(1'-*ortho*-carboranyl)biphenyls

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Cartesian Coordinates for MP2/6-31G* optimised geometries of **7**

Conformer **a** MP2 6-31G* -890.78221868 a.u.

C	-0.70568300	1.46173600	-0.13849300
C	-1.30097500	2.71783200	-0.39603000
C	-0.65048400	3.93510100	-0.24084300
C	0.65101400	3.93513700	0.24086700
C	1.30148300	2.71787200	0.39603700
C	0.70616600	1.46182300	0.13838600
C	-1.76572700	0.36172700	-0.09294300
C	-1.50357400	-1.15830300	0.43965800
C	1.76614000	0.36190800	0.09295200
C	1.50347800	-1.15732000	-0.44070100
B	-2.33851500	-0.11684600	1.49126600
B	-3.37810900	0.80809400	0.41463100
B	-3.03341400	0.32129600	-1.26182000
B	-1.79586000	-0.93142400	-1.23648100
B	-2.78191000	-1.82962100	1.31955500
B	-4.03102800	-0.58376500	1.28289100
B	-4.46512100	-0.30592600	-0.42187200
B	-3.48112900	-1.38962500	-1.43562100
B	-2.43605100	-2.32953700	-0.35434100
B	-4.09762100	-1.95536300	0.14112100
B	3.37903300	0.80784700	-0.41348200
B	3.03313500	0.32036400	1.26248200
B	1.79497500	-0.93168700	1.23601500
B	2.33976900	-0.11591400	-1.49146300
B	3.47974400	-1.39093300	1.43561900
B	4.46498000	-0.30728000	0.42298400
B	4.03172800	-0.58394300	-1.28219100
B	2.78187800	-1.82904900	-1.32018400
B	2.43465700	-2.32957200	0.35325000
B	4.09682500	-1.95620900	-0.14099600

H	-2.33486100	2.74149700	-0.71030000
H	-1.17929500	4.85997300	-0.45471800
H	1.17981700	4.86002800	0.45468800
H	2.33538800	2.74141900	0.71033200
H	-1.93174900	-3.38506600	-0.56432200
H	-4.91741300	-2.81314100	0.22782800
H	-3.84103900	-1.82250600	-2.48345600
H	-5.55189000	0.05085700	-0.75086500
H	-4.78918000	-0.42868600	2.18628900
H	-3.60059900	1.93398600	0.70724400
H	-2.98887400	1.11926700	-2.13986200
H	-1.74224200	0.32830600	2.41564100
H	-0.90510000	-0.97900700	-2.01871500
H	-0.50739500	-1.38904800	0.78049900
H	-2.49609700	-2.55524700	2.21564000
H	2.98857400	1.11823800	2.14062000
H	3.60278000	1.93372700	-0.70516300
H	5.55176100	0.04869900	0.75275500
H	4.79066500	-0.42876400	-2.18494400
H	4.91620300	-2.81439100	-0.22771400
H	2.49622100	-2.55435500	-2.21657500
H	1.92972200	-3.38504500	0.56203400
H	0.50734000	-1.38710100	-0.78236000
H	0.90358700	-0.97879200	2.01755500
H	3.83891600	-1.82461100	2.48337000
H	1.74390100	0.33015000	-2.41566200

Conformer **b** MP2 6-31G* -890.77968323 a.u.

C	-0.69610000	1.41049300	-0.23150600
C	-1.28690900	2.66784100	-0.49314400
C	-0.65834500	3.88978800	-0.28286200
C	0.60152200	3.89610900	0.29845500
C	1.25253700	2.68162000	0.47349400
C	0.70043200	1.42693300	0.12836700
C	-1.77284600	0.32039000	-0.16193900
C	-1.52801200	-1.25838200	0.17575600
C	1.73933200	0.31127200	0.12776500
B	-2.11924300	-0.27865900	1.43764400
B	-3.25453200	0.79628200	0.62314500
B	-3.21260200	0.43896000	-1.11932200
B	-2.05936900	-0.86159300	-1.39990300
B	-2.68903700	-1.94084400	1.19900200
B	-3.84965500	-0.63603200	1.47107400
B	-4.52944100	-0.18439000	-0.11015100
B	-3.78616700	-1.21712000	-1.35659200
B	-2.64861000	-2.30069600	-0.54369300
B	-4.18241600	-1.89310900	0.24742200
B	3.41369700	0.85781700	-0.12034800
B	2.86989000	0.14569300	1.40806600
B	1.68750700	-1.12341600	1.03661200
B	3.36237100	-1.56622600	1.39320200
B	4.42508000	-0.32839400	0.68580300
B	4.22055300	-0.38685600	-1.07334900
B	3.03064400	-1.63454700	-1.45649200
B	2.48544100	-2.37486300	0.06441500
B	4.19141100	-1.89506300	-0.14317500

H	-2.31080400	2.69199000	-0.83781900
H	-1.18671000	4.81211000	-0.50894400
H	1.09492000	4.82166400	0.58239800
H	2.24756500	2.70404500	0.89489500
H	-2.25248200	-3.35610200	-0.91903800
H	-5.03122100	-2.71405800	0.39493900
H	-4.33635400	-1.52821200	-2.36468100
H	-5.62934300	0.25577900	-0.22791600
H	-4.44340700	-0.52920000	2.49663000
H	-3.33308000	1.91040900	1.02216100
H	-3.28387100	1.29319900	-1.93987300
H	-1.36560000	0.05436400	2.29135300
H	-1.29993500	-0.89216400	-2.30810500
H	-0.50644700	-1.57945500	0.28314900
H	-2.31401600	-2.75773700	1.97603100
H	2.71072900	0.83982600	2.35871100
H	3.64265700	1.99626400	-0.33666600
H	5.45038500	0.01603100	1.18107900
H	4.98871500	-0.00807600	-1.89654900
H	5.06627300	-2.69386800	-0.25234800
H	2.97950200	-2.12366900	-2.53763400
H	2.11633900	-3.50529500	0.10484900
H	0.51500300	-1.27247700	-1.37348800
H	0.76639400	-1.26778700	1.77014200
H	3.62200300	-2.12504300	2.41128900
H	2.24008400	0.57393600	-2.16580300
C	2.58221600	-0.00262900	-1.30891900
B	1.49442600	-1.15236000	-0.73367200

Conformer **c** MP2 6-31G* -890.78188347 a.u.

C	-0.71588100	1.41217100	-0.20782000
C	-1.29224000	2.67903600	-0.45382500
C	-0.63447600	3.88810300	-0.26636000
C	0.64066400	3.86762400	0.28017200
C	1.26927500	2.64045100	0.44829700
C	0.68309400	1.39415900	0.12691300
C	-1.79533300	0.33153400	-0.14586000
C	-1.54023000	-1.23799200	0.20040300
C	1.68627500	0.24120800	0.07258500
B	-2.16291900	-0.26511500	1.45047700
B	-3.29154100	0.80000800	0.61401700
B	-3.21486600	0.44317200	-1.12776600
B	-2.04530000	-0.84890400	-1.38843200
B	-2.71313800	-1.93184300	1.20171500
B	-3.88993100	-0.63692500	1.45203300
B	-4.54430300	-0.19154600	-0.14244100
B	-3.76947600	-1.21871600	-1.37495500
B	-2.63597800	-2.29160600	-0.54018900
B	-4.18834200	-1.89741400	0.22224200
B	2.82207800	0.14688700	1.38681800
B	1.70681400	-1.17148400	1.03043400
B	3.40439400	-1.51881300	1.40879500
B	4.39705800	-0.25039600	0.67191600
B	4.20109200	-0.34295600	-1.09026600
B	3.08303600	-1.65568400	-1.45828700

B	2.58550700	-2.39430200	0.08900900
B	4.25813300	-1.83022500	-0.12745700
H	-2.32222600	2.71781700	-0.77940600
H	-1.14819600	4.82120400	-0.48096900
H	1.16161400	4.78313300	0.54737600
H	2.26116100	2.66003200	0.88017100
H	-2.22442900	-3.34429200	-0.90627100
H	-5.03275500	-2.72536000	0.35507600
H	-4.29971100	-1.53638000	-2.39157500
H	-5.64608700	0.23813100	-0.27996100
H	-4.50415600	-0.53466900	2.46596700
H	-3.38758900	1.91353200	1.01110000
H	-3.27276500	1.30190400	-1.94492800
H	-1.42446500	0.07529600	2.31500200
H	-1.26348000	-0.86683000	-2.27738300
H	-0.51558700	-1.54247800	0.32388300
H	-2.34576000	-2.74605000	1.98521700
H	2.67869300	0.91761400	2.27568800
H	3.46541400	1.78407200	-0.25480600
H	5.34975200	0.27932600	1.14443700
H	5.01872800	0.13345100	-1.80857200
H	5.18887300	-2.56802500	-0.19489100
H	3.13402400	-2.26370500	-2.47908500
H	2.28727700	-3.54337800	0.17474100
H	0.51543600	-1.49644400	-1.30616500
H	0.80991000	-1.32980900	1.79246400
H	3.70047000	-2.02125500	2.44533500
H	2.14327500	0.71767900	-2.35622400
B	1.52064900	-1.24903500	-0.74487200
C	3.29234100	0.72042400	-0.15078300
B	2.49936300	0.01593100	-1.46850000

Conformer **d** MP2 6-31G* -890.77755481 a.u.

C	-0.69266600	1.42103400	-0.06321900
C	-1.26272400	2.67088800	-0.39710100
C	-0.60471100	3.88960500	-0.29014500
C	0.68508600	3.89947300	0.21977900
C	1.32158800	2.68271600	0.42850300
C	0.72135100	1.42040900	0.21490600
C	-1.72452600	0.29491000	0.05409000
C	1.79248900	0.32975800	0.14694300
C	1.53039000	-1.22980000	-0.23951000
B	-1.69734600	-1.03002400	-1.05231200
B	-3.06713000	-1.79423700	1.35094300
B	-4.22468900	-0.47401500	1.12799700
B	-4.41509800	-0.21460500	-0.61623000
B	-3.38264200	-1.37813700	-1.46859200
B	-2.53833000	-2.36115300	-0.25819400
B	-4.23073700	-1.86500900	0.01091900
B	3.31320600	0.79267700	-0.57812900
B	3.19366300	0.40943200	1.15560700
B	2.00588000	-0.87505000	1.36942100
B	2.19019700	-0.24173700	-1.45504000
B	3.72530900	-1.26384200	1.38507900
B	4.53747600	-0.22483600	0.18789300
B	3.91264800	-0.63523500	-1.42761500

B	2.71715700	-1.91969200	-1.22614200
B	2.59726500	-2.30905300	0.50728300
B	4.17047800	-1.92017900	-0.21415300
H	-2.29141700	2.70725300	-0.72550500
H	-1.11964200	4.80754100	-0.56045900
H	1.21997500	4.82734600	0.40331400
H	2.35693800	2.71117900	0.73686400
H	-2.20245200	-3.48002500	-0.48348700
H	-5.13292600	-2.63938600	-0.03040200
H	-3.61039200	-1.66472500	-2.59859500
H	-5.33601300	0.28389700	-1.17740900
H	-5.10209000	-0.22346300	1.89118500
H	-3.62146100	1.99730300	0.47112500
H	-2.71301100	0.91218300	-1.96384400
H	-2.12489500	0.43047400	2.52767000
H	-0.84042900	-1.02036500	-1.87268800
H	-0.50139900	-1.56594200	1.21341400
H	-3.09379000	-2.52378800	2.29062200
H	3.23812500	1.25739900	1.98509700
H	3.43823400	1.90760500	-0.96133200
H	5.64065500	0.19012300	0.35580300
H	4.54877300	-0.52057600	-2.42664800
H	5.00779400	-2.75573400	-0.34406800
H	2.35698700	-2.71583200	-2.03138300
H	2.16610900	-3.36323100	0.84555200
H	0.50640400	-1.52270700	-0.39168100
H	1.20730600	-0.89874000	2.24283200
H	4.22944800	-1.60690200	2.40664300
H	1.47587600	0.12279400	-2.33018000
B	-1.51747600	-1.27376200	0.70005700
B	-2.52782000	-0.10357300	1.54582100
B	-3.38964200	0.84673500	0.34987200
C	-2.86036800	0.20813900	-1.14839100